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Modelling Phase Transition Phenomena in Fluids

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ABSTRACT

Phase transitions occur in a variety of physical phenomena ranging from condensation of gases to solidification of liquids. It is of paramount importance to provide an adequate modelling of these phenomena in a thermodynamically consistent way. This paper addresses an introduction into the mathematical modelling of phase transitions in fluids from the perspective of consistently employing a modified Legendre transform of entropy considered as a given function of internal energy and volume. An explicit conservative scheme for incompressible phase transition and an implicit non-conservative scheme based on the fictitious-capacity and lubrication-theory approximations are implemented in MATLAB®. Illustrative numerical simulations are conducted, and some results are verified against an exact benchmark solution.

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Modelling Phase Transition Phenomena in Fluids

Executive Summary

Phase transitions occur in a variety of physical phenomena ranging from condensation of gases to solidification of liquids at certain conditions. It is of paramount importance to provide an adequate modelling of these phenomena in a thermodynamically consistent way. This paper addresses an introduction into the mathematical modelling of phase transitions in fluids from the perspective of consistently employing a modified Legendre transform of entropy considered as a given function of internal energy and volume (primary variables). The Legendre transform depends naturally on the absolute temperature and pressure (potential variables), and coincides with the Gibbs free energy. When entropy ceases to be a strictly concave function of the primary variables, the derivatives of the Gibbs free energy become discontinuous with respect of the potential variables at some phase-transition line. These derivatives define the primary variables at equilibrium, and their jumps are the latent energy and volume of the phase transition. The second-order derivatives of the Gibbs free energy, defining heat capacity, compressibility and expansivity, exhibit delta-function singularities at the phase-transition line. The main feature of a Legendre transform is concavity (or convexity) from which a bunch of important consequences are readily obtained.

An explicit conservative scheme for incompressible phase transition and an implicit non-conservative scheme based on the fictitious-capacity and lubrication-theory approximations are implemented in MATLAB®. Illustrative numerical simulations are conducted, and some results are verified against an exact benchmark solution.

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CFD Computational Fluid Dynamics

FEM Finite Element Method

FVM Finite Volume Method

SUPG Streamline Upwind Petrov–Galerkin

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1 Introduction

Phase transitions occur in a variety of physical phenomena ranging from the condensation of gases to solidification of liquids at certain conditions. It is of paramount importance to provide an adequate mathematical modelling of these phenomena in a thermodynamically consistent way. The main objective of this paper is to present an introduction into the thermodynamics of phase transitions using the useful mathematical apparatus of Legendre transform [Zia, Redish & McKay 2009], formulate mathematical models starting from the most general one, and describe numerical schemes. Illustrative numerical simulations are conducted, and some schemes are verified against an exact solution.

The Legendre transform is commonly employed in *Classical Mechanics* [Arnold 1989] and *Thermodynamics* [Callen 1985], however its power is not always utilized in full as the traditional approach of teaching *Physics* is historically dominated. We will show here how many important consequences can be derived economically in a straightforward manner from the proper definition of Gibbs free energy employing the Legendre transform whose use is inextricably linked with the *Maximum Entropy Principle.*

For the sake of simplicity, we confine ourselves to phase transitions in fluids composed of a single species, which comprise liquids and their vapours (gases), and can be modelled by a two-parametric thermodynamic system. The latter means that only two independent variables define the thermodynamic state of the system, such as energy and volume, the primary variables, or temperature and pressure, the potential variables. An extension of this approach to fluids composed of several species is straightforward.

Though both types of variables are generally equivalent for the description of a physical phenomenon, the transformation from the primary to potential variables is not always invertible. This particularly happens when phase transitions take place. Indeed, a small variation in temperature and pressure across the phase-transition line in the phase diagram results in large changes in energy and volume. These changes are, respectively, the latent energy and latent volume of the thermodynamic system undergoing a phase transition. For an incompressible phase transition, the latent volume vanishes and the latent energy becomes equal to the latent heat.

The typical phase diagram in the (T, p)-plane, where T denotes the absolute temperature and p pressure, is shown in Figure 1. Two special states, called respectively the *critical point* and *triple point*, are depicted. The *critical point* is the point beyond which there is no distinction between liquid and its vapour. In other words, in the supercritical region there is a single fluid phase with continuous dependence of energy and volume on pressure and temperature. The *triple point* is the unique pressure and temperature for which three phases of a substance coexist. The sublimation, fusion and vaporisation lines branching from the *triple point* are shown. Note that additional phase transitions can take place in the solid state, which cannot be described by a two-parametric thermodynamic system.

In many practical applications the solid-liquid phase transitions can be assumed incompressible, and therefore the corresponding thermodynamic system becomes one-parametric. Indeed, the densities of the two phases do not change dramatically, and this is reflected by the fact that the fusion line is nearly vertical for most materials. This simplifying assumption allows one to model incompressible phase transitions by the solution of the Stefan problem [Meirmanov 1992] which is decoupled from the fluid motion. The latter
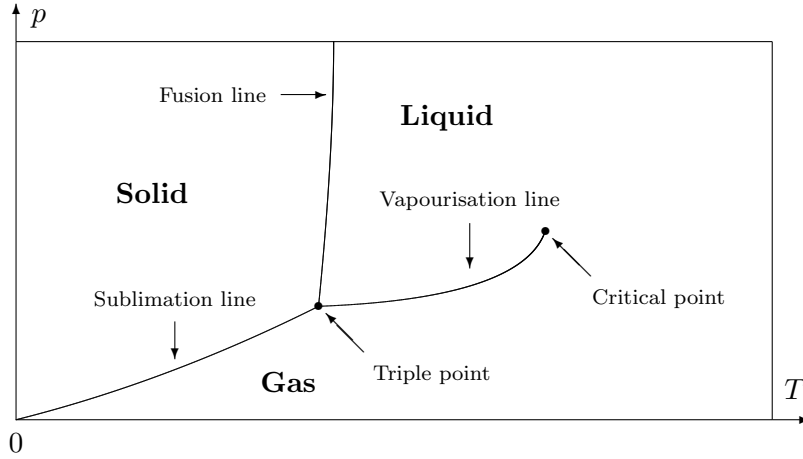
Figure 1: Schematic of a phase diagram

means that the velocity field can be set zero, and only the balance of energy constitutes the Stefan model. In contrast to this the liquid-gas phase transitions occurring at the vapourisation line are more complex in nature as the corresponding thermodynamic system is genuinely two-parametric, and there is no way to decouple fluid motion [Kutateladze & Borishanskii 1966, Kandlikar 1999]. The model becomes more complicated if additionally the effect of surface tension is taken into account [Antanovskii 1996].

2   Elements of thermodynamics

For ready reference, we recall the basic notions and principles of thermodynamics [Fermi 1937, Reif 1965, Kittel 1969]. The main attention is paid to the rigorous definition of all the necessary variables starting with entropy dependence on macroscopic primary variables and employing a Legendre transform. Then we discuss the thermodynamics of phase transitions and provide an illuminating example using the van der Waals equation of state.

2.1   General principles

Fluids composed of a single species, such as pure water in either liquid or vapour phase, can be described by a two-parametric thermodynamic system. This means that two independent variables, the internal energy E and volume V, define the state of a substance of some fixed mass M or, equivalently, of some fixed number of particles N. These parameters are reliably controlled in an experiment, and a system with given E and V is called an *isolated thermodynamic system*. In other words the isolated thermodynamic system is not allowed to exchange energy with the environment or do any work.

The primary variables (E, V) define the macrostate of the thermodynamic system. However, these variables do not determine the system's microstates. It was the greatest idea by Rudolf Clausius, one of the founders of *Thermodynamics*, to introduce entropy S and make it responsible for determining the most probable microstates compatible with the

given macrostate through the celebrated *Maximum Entropy Principle*. A particular material has its unique dependence of entropy on the primary variables. In other words, to the first approximation, entropy is assumed to be the only additional variable that defines the microscopic structure of a physical material. In particular, the dependence $S = S(E, V)$ is capable of describing all the observable physical phenomena in fluids including phase transitions. In this sense *Thermodynamics* is a very economic theory with excellent applications to the real world.

In this connection it is worthwhile noting that a confusion commonly arises from the naïve interpretation of the *Maximum Entropy Principle* by stating that the entropy of an isolated thermodynamic system tends to a maximum. This statement obviously contradicts the dependence $S = S(E, V)$ which tells us that the entropy does not have a freedom to achieve either a maximum or a minimum. Indeed, it is completely determined by the macrostate through the given dependence $S = S(E, V)$. This motivates the inclusion of the rigorous formulation of the *Maximum Entropy Principle* below to avoid confusion.

The modern definition of entropy due to Ludwig Boltzmann is given by the following expression

$$S = k_B \log W \tag{1}$$

where k_B is Boltzmann's constant, W is the number of microstates consistent with the given macrostate (also called the degeneracy of the energy level), and the logarithm is natural. This expression is very useful in *Statistical Mechanics*, the theory aimed at deriving the macroscopic properties of a material from a knowledge of molecule interaction, that boils down to calculating the degeneracy W of quantum states as a function of E and V. The greater the degeneracy W the less information about the system's microstate at particular instant is available, so entropy measures the missing information about the system. It is postulated in *Thermodynamics* and *Statistical Mechanics* that all the microstates are equally probable.

The reason for using the logarithm in the definition of entropy will be clear from the following thought experiment [Kittel 1969]. Let us consider two isolated thermodynamic systems $\mathcal{D}_a$ and $\mathcal{D}_b$ depicted in Figure 2. The corresponding numbers of microstates are well defined in terms of energies and volumes. Let $\mathcal{D}_c$ be the logical union of the systems $\mathcal{D}_a$ and $\mathcal{D}_b$, which is also isolated. In this case $E_c = E_a + E_b$, $V_c = V_a + V_b$, $W_c = W_a W_b$ and therefore $S_c = S_a + S_b$. In other words, entropy behaves like an additive (extensive) variable, such as energy or volume.

Let us now allow the two thermodynamic systems to exchange energy and momentum (work) but not mass. This means that we are not maintaining the energy and volume of each open system, but the total energy and volume of the combined isolated system $\mathcal{D}_c = \mathcal{D}_a \cup \mathcal{D}_b$. The total energy and volume are equal to the sums of the initial energies and volumes of the subsystems $\mathcal{D}_a$ and $\mathcal{D}_b$ before contact provided that the interfacial energy is negligibly small.[1] In other words,

$$E_c = E_a^o + E_b^o, \quad V_c = V_a^o + V_b^o, \tag{2}$$

where (E_a^o, V_a^o) and (E_b^o, V_b^o) are the initial energies and volumes of the subsystems $\mathcal{D}_a$ and $\mathcal{D}_b$, respectively.

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[1]This is not the case when the effect of capillarity is taken into account.
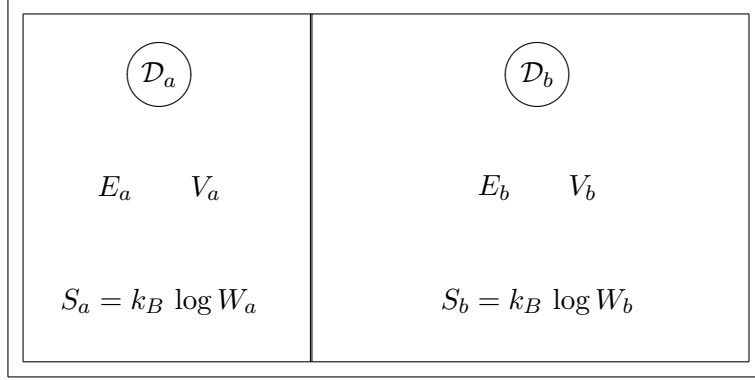
Figure 2:   Two thermodynamic systems

The number of microstates of the combined system is equal to the following sum of the products

$$W_c\left(E_c, V_c\right) = \sum W_a\left(E_a, V_a\right) W_b\left(E_b, V_b\right) \tag{3}$$

where the summation is taken over all the possible values of energy and volume satisfying the constraints

$$E_a + E_b = E_c \ \left(\equiv E_a^o + E_b^o \right), \quad V_a + V_b = V_c \ \left(\equiv V_a^o + V_b^o \right). \tag{4}$$

Obviously, the product $W_a\left(E_a^o, V_a^o\right) W_b\left(E_b^o, V_b^o\right)$ is present in the sum (3) because the above constraints admit it, and therefore the total entropy satisfies the strict inequality

$$S_c\left(E_c, V_c\right) > S_a\left(E_a^o, V_a^o\right) + S_b\left(E_b^o, V_b^o\right). \tag{5}$$

This fact is not surprising since two independent sets of constraints for the thermodynamic systems are replaced with the single set of constraints (4) for the combined system, and therefore the number of microstates of the combined system increases due to extra freedom.

The *Maximum Entropy Principle* states that a thermodynamic equilibrium is attained at those pairs (E_a, V_a) and (E_b, V_b) which provide the maximum value of some product in (3). In other words, we arrive at the maximisation problem

$$S_a\left(E_a, V_a\right) + S_b\left(E_b, V_b\right) \to \max \tag{6}$$

under the constraints (4), which immediately gives the necessary conditions for thermodynamic equilibrium[2]

$$\frac{\partial S_a\left(E_a, V_a\right)}{\partial E} = \frac{\partial S_b\left(E_b, V_b\right)}{\partial E} \equiv \frac{1}{T}, \quad \frac{\partial S_a\left(E_a, V_a\right)}{\partial V} = \frac{\partial S_b\left(E_b, V_b\right)}{\partial V} \equiv \frac{p}{T}. \tag{7}$$

Here the definitions of the absolute temperature T and pressure p are introduced through the derivatives of entropy, which are commonly called potential variables conjugate to energy E and volume V. The potential variables (T, p) are equal in each thermodynamic system in contact thus providing the condition for thermodynamic equilibrium.

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[2]Though W is integer, we assume that the resulting function $S = S(E, V)$ can be differentiated.

For given functions $S_a(E, V)$ and $S_b(E, V)$, four unknowns (E_a, V_a, E_b, V_b) can be in principle determined from the four equations (4) and (7). Alternatively, each pair (E_a, V_a) and (E_b, V_b) can be determined in terms of T and p if these are given. Such a situation arises when one thermodynamic system $(\mathcal{D}_a)$ is significantly smaller than the other one $(\mathcal{D}_b)$. The larger system plays the rôle of a reservoir of heat and work. Assuming $E_a \ll E_b$ and $V_a \ll V_b$, the problem (6), equivalently written in the form

$$S_a\left(E_a, V_a\right) + S_b\left(E_c - E_a, V_c - V_a\right) \to \max, \tag{8}$$

reduces to the approximate problem

$$S_a\left(E_a, V_a\right) - \frac{E_a + p\,V_a}{T} \to \max. \tag{9}$$

Here in the Taylor series expansion of the reservoir entropy $S_b\left(E_c - E_a, V_c - V_a\right)$ we retain only the linear terms and drop the constant term $S_b\left(E_c, V_c\right)$ which obviously does not affect the solution. In this case the absolute temperature T and pressure p are the properties of the reservoir, which are assumed constant regardless of small exchange of energy and volume with the attached thermodynamic system. Of course, the necessary conditions for the solution of the problem (9) are as follows

$$\frac{\partial S_a\left(E_a, V_a\right)}{\partial E} = \frac{1}{T}, \qquad \frac{\partial S_a\left(E_a, V_a\right)}{\partial V} = \frac{p}{T}, \tag{10}$$

which are in agreement with (7).

It is worthwhile emphasizing that, for a thermodynamic system composed of a huge number of particles, the following equality holds with a very high accuracy

$$S_c\left(E_c, V_c\right) = S_a\left(E_a, V_a\right) + S_b\left(E_b, V_b\right). \tag{11}$$

The approximate equality (11) takes place for thermodynamic subsystems in contact only after the equilibrium is achieved. This is in contrast with the strict inequality (5).

This purely statistical observation allows one to assume that entropy is an extensive thermodynamic variable. From this point it makes sense to talk about the specific energy e, volume v and entropy s defined by the formulae

$$e = \frac{E}{M}, \quad v = \frac{V}{M}, \quad s = \frac{S}{M}. \tag{12}$$

(Alternatively, we can introduce molar properties

$$e' = \frac{N_A\,E}{N}, \quad v' = \frac{N_A\,V}{N}, \quad s' = \frac{N_A\,S}{N}, \tag{13}$$

where N_A is Avogadro's number.)

The equation of state is now reformulated in terms of the specific thermodynamic properties: $s = s(e, v)$. The subscripts identifying thermodynamic subsystems are dropped from this point. The definitions of temperature and pressure do not change as they are intensive variables

$$\frac{\partial s\left(e, v\right)}{\partial e} = \frac{1}{T}, \qquad \frac{\partial s\left(e, v\right)}{\partial v} = \frac{p}{T}. \tag{14}$$

The second law of *Thermodynamics* immediately follows from the above definitions

$$T\,\mathrm{d}s = \mathrm{d}e + p\,\mathrm{d}v\,. \tag{15}$$

This invariant form of the second law does not imply the original set of independent variables any more.

It is worthwhile stressing that the absolute temperature T is always positive. As demonstrated in *Statistical Mechanics*, the latter is due to the fact that the spectrum of energy of fluids does not have an upper bound. In particular, the maximum entropy principle (9) is equivalent to the following

$$e + p\,v - T\,s(e,v) \to \min \tag{16}$$

where the (specific) primary variables e and v are free but the potential variables T and p are fixed. Of course, at the point of minimum we get (14).

In many textbooks on *Thermodynamics* the (specific) Gibbs free energy is defined by the expression

$$g = e + p\,v - T\,s \tag{17}$$

which is poorly motivated outside the context of the *Maximum Entropy Principle*. The more rigorous definition we adopt here is in the form of the modified Legendre transform

$$g(T,p) = \min_{e,\,v}\left[e + p\,v - T\,s(e,v)\right]\,. \tag{18}$$

The definition (18) reflects the *Maximum Entropy Principle* applied to a small thermodynamic system in contact with a reservoir of heat and work, and clearly demonstrates that the absolute temperature T and pressure p are the variables on which the Gibbs free energy naturally depends.

The Gibbs free energy is also called the *free enthalpy*, and the term *free energy* is usually reserved for the (specific) Helmholtz free energy defined by the formula

$$f(T,v) = \min_{e}\left[e - T\,s(e,v)\right]\,. \tag{19}$$

The Helmholtz free energy is useful in describing a thermodynamic system of fixed volume (isochoric process) attached to a reservoir of heat at given temperature T.

The most important consequence of the definition (18) is the fact that $g(T,p)$ is a continuous concave function of T and p. This conclusion directly follows from the observation that a function defined as the minimum of a family of linear functions is concave. Continuity follows from the general fact that the minimum of a family of continuous functions (linear functions in our case) is a continuous function. Likewise, the definition (19) implies that $f(T,v)$ is a continuous concave function of T at any fixed v. To illustrate this just draw a collection of straight lines on a plane and fit a curve below them, tangent to each line.

Assuming that $g(T,p)$ is a smooth function, we immediately arrive at the dependence of the primary variables on the potential variables

$$e = g - T\,\frac{\partial g}{\partial T} - p\,\frac{\partial g}{\partial p}\,, \quad s = -\frac{\partial g}{\partial T}\,, \quad v = \frac{\partial g}{\partial p}\,. \tag{20}$$

Of course, all the primary variables (including entropy) in (20) are now functions of T and p. Note that, with the help of the Legendre transform, the solution of the system of nonlinear equations (14) is readily obtained by simple differentiation. This procedure automatically singles out the unique solution to (14) consistent with the *Maximum Entropy Principle*. It is worthwhile noting that the map

$$(e, v) \mapsto \left(\frac{\partial s}{\partial e}, \frac{\partial s}{\partial v} \right) \equiv \left(\frac{1}{T}, \frac{p}{T} \right) \tag{21}$$

is also called a Legendre transform (or a contact transformation). However, in this weak form the Legendre transform is not very useful in thermodynamics.

The map (21) may not be invertible *a priori*. However, it is invertible if the entropy dependence $s = s(e, v)$ is a strictly concave function. The later means that the following strict inequalities take place

$$\frac{\partial^2 s}{\partial e^2} < 0, \quad \frac{\partial^2 s}{\partial v^2} < 0, \quad \frac{\partial^2 s}{\partial e^2} \frac{\partial^2 s}{\partial v^2} > \left(\frac{\partial^2 s}{\partial e \, \partial v} \right)^2 . \tag{22}$$

In this case the Gibbs free energy is also a strictly concave function

$$\frac{\partial^2 g}{\partial T^2} < 0, \quad \frac{\partial^2 g}{\partial p^2} < 0, \quad \frac{\partial^2 g}{\partial T^2} \frac{\partial^2 g}{\partial p^2} > \left(\frac{\partial^2 g}{\partial T \, \partial p} \right)^2 . \tag{23}$$

Moreover, the original entropy function $s(e, v)$ coincides with its double Legendre transform $\hat{s}(e, v)$ given by the formula

$$\hat{s}(e, v) = \min_{T, p} \left[\frac{e + p \, v - g(T, p)}{T} \right] . \tag{24}$$

In other words, the Legendre transform on concave functions is involutive: $\hat{s}(e, v) \equiv s(e, v)$.

From (23) a bunch of important consequences will be now deduced. Let us introduce the specific heat capacity at constant pressure c_p, isothermal compressibility a_T, and isobaric thermal expansivity b_p by the formulae

$$c_p = T \, \frac{\partial s}{\partial T}, \quad a_T = -\frac{1}{v} \, \frac{\partial v}{\partial p}, \quad b_p = \frac{1}{v} \, \frac{\partial v}{\partial T} . \tag{25}$$

These thermodynamic properties are measurable in experiments aimed at determining the equation of state of a particular material. The heat capacity c_p and isothermal compressibility a_T are always positive since the function $g(T, p)$ is strictly concave

$$c_p \equiv -T \, \frac{\partial^2 g}{\partial T^2} > 0, \quad a_T \equiv -\frac{1}{v} \, \frac{\partial^2 g}{\partial p^2} > 0 . \tag{26}$$

In contrast to this, nothing prevents the isobaric thermal expansivity b_p to have any sign. For example, water at standard pressure condition ($p = 0.1 \, \mathrm{MPa}$) has a local maximum of density with respect of temperature near $T = 277 \, \mathrm{K}$ ($4°\mathrm{C}$). However, due to the identity

$$b_p \equiv \frac{1}{v} \, \frac{\partial^2 g}{\partial T \, \partial p} , \tag{27}$$

the last condition (23) imposes the bound

$$|b_p| < \sqrt{\frac{a_T \, c_p}{v \, T}} \, . \tag{28}$$

The properties c_p, a_T and b_p as functions of T and p are not independent but must satisfy compatibility conditions resulting from the fact that all of them are defined in terms of the single function $g(T, p)$. For example, the following identities hold

$$\frac{\partial(c_p/T)}{\partial p} + \frac{\partial(b_p \, v)}{\partial T} \equiv 0 \, , \quad \frac{\partial(a_T \, v)}{\partial T} + \frac{\partial(b_p \, v)}{\partial p} \equiv 0 \, . \tag{29}$$

This fact is very useful as significantly reduces the number of experiments for determining the equation of state of a material in question.

Let c_v be the specific heat capacity at constant volume. It is straightforward to prove the equality [Reif 1965]

$$c_p - c_v = \frac{b_p^2 \, T \, v}{a_T} \tag{30}$$

which particularly ensures the inequality $c_p > c_v$. The strict concavity of $g(T, p)$ guarantees that c_v is positive. Indeed, direct calculations result in the inequality

$$c_v \equiv \frac{T}{a_T \, v} \left[\frac{\partial^2 g}{\partial T^2} \frac{\partial^2 g}{\partial p^2} - \left(\frac{\partial^2 g}{\partial T \, \partial p} \right)^2 \right] > 0 \, . \tag{31}$$

(This result can be also obtained from the strict concavity of the Helmholtz free energy with respect of T because

$$s = -\frac{\partial f}{\partial T} \, , \quad c_v = T \, \frac{\partial s}{\partial T} \equiv -T \, \frac{\partial^2 f}{\partial T^2} > 0 \, . \tag{32}$$

Here the independent variables are T and v.)

The positivity of a_T, c_p and c_v is an important consequence of the definition of the Gibbs free energy in terms of the Legendre transform. In many circumstances this allows one to prove Le Châtelier's principle which states [Reif 1965]:

> *If a system is in stable equilibrium, then any spontaneous change of its parameters must bring about processes which tend to restore the system to equilibrium.*

A thermodynamically consistent mathematical model for real-world physical phenomena must respect this important principle in the first place.

2.2 Phase transitions

Phase transitions of the first kind are characterized by an abrupt dependence of the primary variables (e, v) on the potential variables (T, p). If the entropy dependence $s = s(e, v)$ is a strictly concave function of e and v, then the Legendre transform is also a strictly

concave function, and in particular there will be an invertible mapping between (T, p) and (e, v) in terms of the Gibbs free energy.

It is conceivable from the above that, within this framework, phase transitions can be modelled under the assumption that $s(e, v)$ is not a concave (or strictly concave) function of the primary variables. In this case the function $g(T, p)$ will have discontinuous partial derivatives, and therefore a discontinuous dependence of the primary variables on the potential variables will be observed. The jumps of the primary variables is nothing else than the latent energy and latent volume of phase transition. This kind of singularities of Legendre transforms is analysed in the theory of catastrophes [Bröker 1975, Arnold, Gusein-Zade & Varchenko 1985].
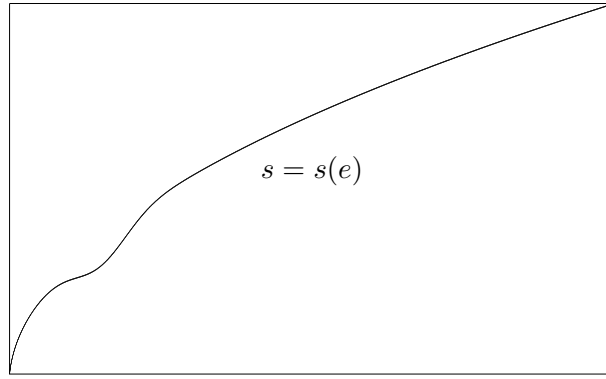

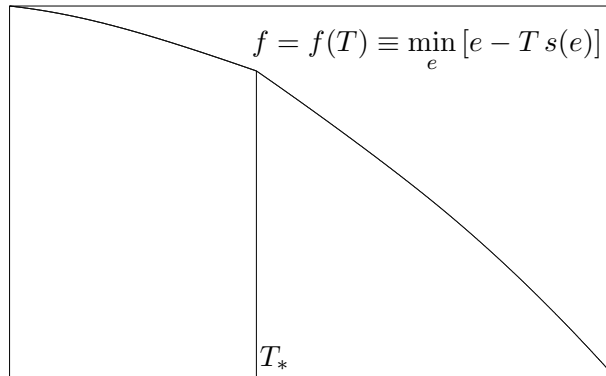*Figure 3: Entropy versus energy*

Figure 4: Free energy versus temperature

Let us illustrate the described discontinuous behaviour using an example of an incompressible (one-parametric) phase transition. We suppress the dependence on v and consider a non-concave dependence of entropy on energy as shown in Figure 3. The graph contains a local region of non-concavity (the 'dimple'). The calculated Helmholtz free energy is shown in Figure 4. Obviously, some interval of energy e is Legendre transformed to a single point, the phase-transition temperature T_*, where the free energy has a kink. Subsequently, energy as a function of temperature exhibits a jump at the phase-transition temperature as shown in Figure 5. This jump is the latent energy. The double Legendre transform of
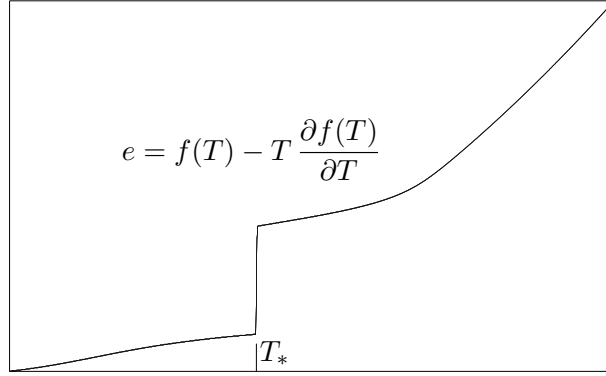
$$e = f(T) - T\frac{\partial f(T)}{\partial T}$$

T_*

Figure 5:   Energy versus temperature

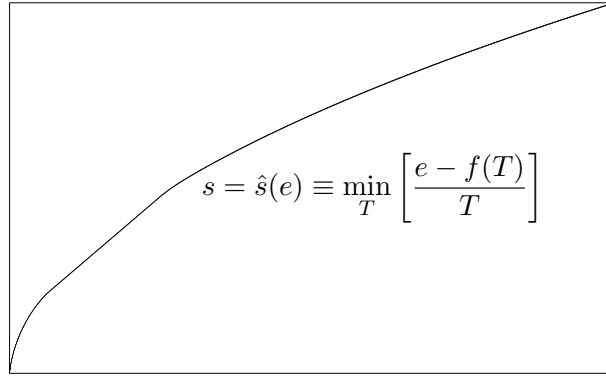$$s = \hat{s}(e) \equiv \min_T \left[\frac{e - f(T)}{T}\right]$$

Figure 6:   Double Legendre transformed entropy versus energy

entropy is shown in Figure 6. This function of energy is concave but not strictly concave as the graph has a region with constant slope which removes the 'dimple' of the original function. Outside of this region the original and 'corrected' entropy functions coincide.

It is worthwhile emphasizing that the Legendre transform maps the one-dimensional interval in the space of energies to the zero-dimensional point (T_*) in the space of temperatures. In other words, one dimension is lost under the Legendre transformation of a non-concave entropy.

Likewise, phase transitions in a two-parametric system kept in contact with a reservoir at given temperature T and pressure p occur at a phase-transition line in the (T, p)-plane. In other words, some two-dimensional region in the (e, v)-plane is Legendre transformed to a one-dimensional line in the (T, p)-plane.[3] In practice this phase-transition line is parametrized either by temperature, $p = p_*(T)$, or by pressure, $T = T_*(p)$. On the vapourisation line the function $p = p_*(T)$ is called the vapour pressure, and on the fusion line the function $T = T_*(p)$ is the pressure-dependent fusion temperature. Both approaches can be unified by assuming that the points of the phase-transition line (T_*, p_*) are parametrized by some convenient parameter or given implicitly by some equation $\varphi(T, p) = 0$ in the (T, p)-plane. Of course, in the case of a vapourisation line, this equation makes sense up

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[3]Theoretically, this line can collapse to a point in a degenerate case.

to the critical state.

Due to the global continuity of $g(T, p)$, the second law of thermodynamics (15) is valid in finite variations when the phase-transition line is crossed at a point (T_*, p_*), namely

$$T_* \, \delta s = \delta e + p_* \, \delta v \,. \tag{33}$$

Here δs, δe and δv are the latent entropy, energy and volume, respectively. Note that, since a phase transition is a reversible thermodynamic process, the latent entropy, energy and volume change their signs if the phase-transition line is crossed in the opposite direction. To avoid this ambiguity the latent properties are uniquely defined by requiring that the phase-transition line is crossed in a direction from solid to liquid or from liquid to gas (vapour) phases. The term $T_* \, \delta s$ is the latent heat, and it is natural to call the product $p_* \, \delta v$ the latent work.

Since the differential $\mathrm{d}g(T, p)$ evaluated at a tangent element (dT_*, dp_*) to the phase-transition line is the same for both phases, the Clausius–Clapeyron equation [Reif 1965] is immediately derived

$$\frac{\mathrm{d}p_*}{\mathrm{d}T_*} = \frac{\delta s}{\delta v} \,. \tag{34}$$

Equations (33) and (34) allow one to express the latent energy and latent volume in terms of (T_*, p_*) and δs, namely

$$(\delta e, \delta v) = \left(T_* - p_* \frac{\mathrm{d}T_*}{\mathrm{d}p_*}, \frac{\mathrm{d}T_*}{\mathrm{d}p_*} \right) \delta s \,. \tag{35}$$

The phase-transition diagram and the latent heat are measured in experiments for a range of temperatures, and therefore δe and δv are completely determined by (35). Of course, since the primary variables are discontinuous, the properties c_p, a_T and b_p exhibit delta-function singularities at the phase-transition line.

When modelling fluid flows with phase transitions, it is more consistent to use the double Legendre transform (24) beforehand as the fundamental equation of state. With entropy thus defined, it is straightforward to check that the Jacobian of the transformation $(e, v) \mapsto (T, p)$ is singular at phase coexistence states, *i.e.*

$$\det \frac{\partial(T, p)}{\partial(e, v)} = 0 \,. \tag{36}$$

Indeed, we have the conditions for (non-strict) concavity

$$\frac{\partial^2 \hat{s}}{\partial e^2} \le 0 \,, \quad \frac{\partial^2 \hat{s}}{\partial v^2} \le 0 \,, \quad \frac{\partial^2 \hat{s}}{\partial e^2} \frac{\partial^2 \hat{s}}{\partial v^2} \ge \left(\frac{\partial^2 \hat{s}}{\partial e \, \partial v} \right)^2 \,, \tag{37}$$

which tell us that the Jacobian (36) vanishes if either of inequalities becomes an equality.

The images of the points at which the Jacobian of a transformation is singular are called critical values. According to Sard's theorem [Sard 1942, Sternberg 1964] the set of the critical values of any (differentiable) map has zero measure. In our case of a two-parametric thermodynamic system, the critical values of the Legendre transform constitute the vapour

pressure curve whose area (Lebesgue measure) is obviously zero. Sard's theorem provides a mathematical foundation for Gibbs' phase rule [Gibbs 1948] though does not prove it in full. Strictly speaking, Gibbs' phase rule is valid for the general configuration only. For example, it is straightforward to design a degenerate entropy dependence $s = \hat{s}(e, v)$ which maps the phase coexistence domain in the primary variables to a single point in the potential variables by means of the Legendre transform. However, such an equation of state may model no real fluid.

The described approach is the most straightforward and thermodynamically consistent way to model phase transitions. Phase transitions discussed here so far belong to the class of first-order phase transitions. Second-order phase transitions are characterized by a continuous behaviour of the primary variables on the potential variables but some other derived properties, such as heat capacity, diverge. In this case there is no latent heat anymore. Technically, this situation can be modelled by assuming that the entropy $s = s(e, v)$ is not strictly concave at some set in the (e, v)-plane with empty interior, such as a line or a point.

Second-order phase transitions also take place in conventional fluids when pressure and temperature are carefully controlled in such a manner that the point (T, p) of the phase diagram passes through the critical point (T_c, p_c), being transversal (not tangent) to the phase-transition line. The theoretical background of critical phenomena is presented in many monographs [Binney et al. 2002].

2.3 The van der Waals equation of state

Consider the thermal equation of state of the van der Waals fluid

$$p(T, v) = \frac{R\,T}{v - b} - \frac{a}{v^2} \tag{38}$$

where R is the specific gas constant, and a and b are positive parameters. The specific volume v must be greater than b. Formula (38) reduces to the thermal equation of state of an ideal gas when both a and b vanish.

The critical state of the van der Waals fluid is obtained from the following equations to be solved simultaneously

$$\frac{\partial p(T, v)}{\partial v} = 0\,, \quad \frac{\partial^2 p(T, v)}{\partial v^2} = 0\,, \tag{39}$$

which have the solution

$$T_c = \frac{8a}{27b\,R}\,, \quad p_c = \frac{a}{27b^2}\,. \tag{40}$$

The above formulae are expressed for a and b in terms of the critical temperature T_c and pressure p_c as follows

$$a = \frac{27R^2\,T_c^2}{64p_c}\,, \quad b = \frac{R\,T_c}{8p_c}\,. \tag{41}$$

The critical parameters T_c and p_c are quite reliably measured for various materials, and thus the van der Waals equation of state is completely specified given the specific gas constant R.

The second law of thermodynamics (15) requires that the specific heat at constant volume is a function of temperature only: $c_v = c_v(T)$. This is proved in exactly the same way as for an ideal gas. Everything that matters is the linearity of $p(T, v)$ with respect of T. The dependence $c_v = c_v(T)$ is called the caloric equation of state.

The thermal and caloric equations of state define entropy $s = s(e, v)$ up to a constant. Indeed, let us calculate the anti-derivative

$$u(T) = \int c_v(T)\, \mathrm{d}T\,, \tag{42}$$

and then calculate its inverse function $u^{-1}(e)$. The inverse function exists because $c_v > 0$. Then calculate the anti-derivative

$$w(e) = \int \frac{\mathrm{d}e}{u^{-1}(e)} \tag{43}$$

in terms of which the dependence of entropy on the primary variables is established

$$s(e, v) = s_o + R \log \frac{v - b}{v_o - b} + w\left(e + \frac{a}{v}\right) - w\left(e_o + \frac{a}{v_o}\right) \tag{44}$$

where e_o, v_o and s_o are some reference parameters. For constant c_v (perfect fluid), it reduces to the analytic expression

$$s(e, v) = s_o + R \log \frac{v - b}{v_o - b} + c_v \log \frac{e + a/v}{e_o + a/v_o}\,. \tag{45}$$

This function is not concave with respect of (e, v) as can be checked by direct differentiation, though it is strictly concave with respect of e for any fixed v.

In order to compute the Gibbs free energy $g(T, p)$, it suffices to solve the following cubic equation

$$p\, v^3 - (R\, T + b\, p)\, v^2 + a\, v - a\, b = 0 \tag{46}$$

for volume v at given T and p, and then find the minimum value of the expression

$$c_v\, T - \frac{a}{v} + p\, v - T\left[s_o + R \log \frac{v - b}{v_o - b} + c_v \log \frac{c_v\, T}{e_o + a/v_o}\right] \tag{47}$$

over the real roots. This minimum value is equal to $g(T, p)$.

Let us specify the van der Waals equation of state for water. In this case we choose $R = 462\,\mathrm{J/K/kg}$, $c_v = 1600\,\mathrm{J/K/kg}$, $T_c = 647\,\mathrm{K}$ and $p_c = 22\,\mathrm{MPa}$. Strictly speaking, c_v is quite different for water and its steam [Lide 1999]. Nevertheless, to capture the qualitative behaviour of phase transitions in water, we assume that it is constant (perfect fluid).

Figure 7 displays the van der Waals equation of state (38) for two subcritical and one supercritical temperature values. On the supercritical isotherm, pressure monotonically
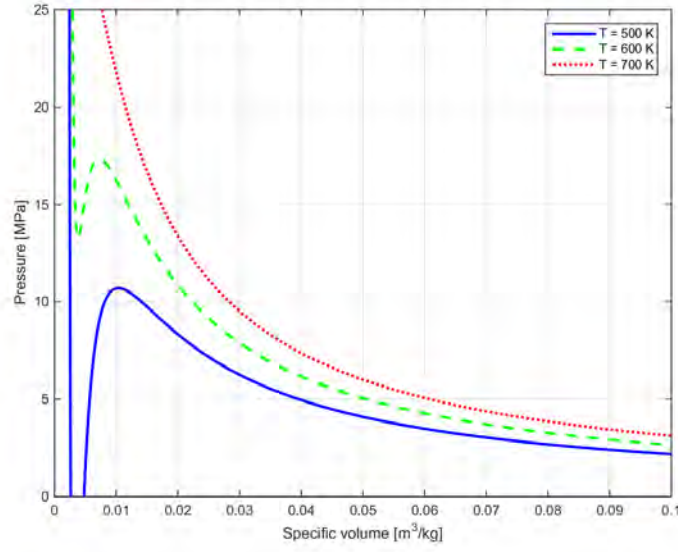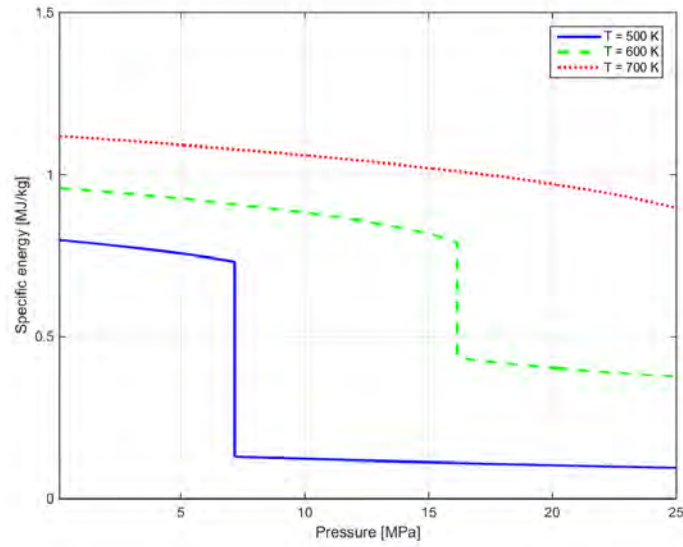
Figure 7: The van der Waals equation of state

Figure 8: Energy-pressure isotherms

decreases with increasing specific volume, whereas the subcritical isotherms are not monotone. Moreover, pressure becomes even negative that does not make sense from the physical point of view. This shortcoming is corrected by replacing the analytic expression for entropy with its double Legendre transform (24). Alternatively, we can employ the Gibbs free energy and calculate the primary variables in terms of the potential variables.

Figure 8 shows energy-pressure isotherms. As is expected, specific energy changes abruptly

at some pressure and given subcritical temperature defining the isotherm. The latent energy diminishes with increasing temperature until it vanishes beyond the critical point.
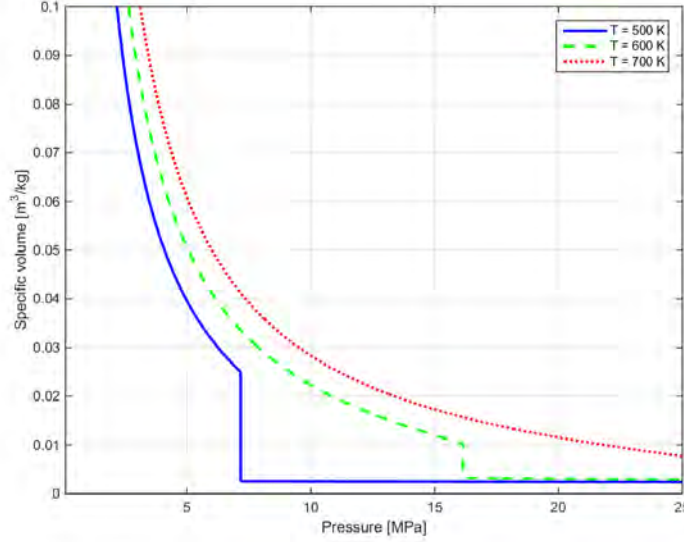

Figure 9: Volume-pressure isotherms

Figure 9 shows volume-pressure isotherms. In fact, after swapping the coordinate axes, these are the pressure-volume isotherms (the van der Waals equation of state) shown in Figure 7 but obtained from the Gibbs free energy or, equivalently, from the double Legendre transform of entropy. In contrast to the van der Waals equation of state, these isotherms are monotonic, exhibiting an abrupt change in specific volume. It is straightforward to verify that these isotherms can be obtained by applying Maxwell's equal area rule [Maxwell 1875, Reif 1965].

The specific heat capacities as functions of temperature at standard pressure are shown in Figure 10. The delta-function singularity of the specific heat capacity at constant pressure (c_p) is depicted. Since we model water and its vapour by a perfect fluid, the specific heat capacity at constant volume (c_v) is constant. In real fluids both heat capacities exhibit similar types of singularities which are not captured by this model. It is also seen that the vapourisation temperature is greatly underpredicted. This is obviously a shortcoming of the van der Waals equation of state.

The vapour pressure curve for the van der Waals fluid is shown in Figure 11. This is the phase diagram in potential variables. As is expected, the vapourisation line ends at the critical point (T_c, p_c) depicted by the filled circle. The phase diagram in the plane of the primary variables is shown in Figure 12. The coexistent states of the liquid-vapour phases correspond to the shaded region. The slopes of the straight lines are given by the relations (35). This two-dimensional region of coexistent phases is mapped to the one-dimensional vapourisation line by the Legendre transform. The critical state in the primary variables mapped to (T_c, p_c) by the Legendre transform is depicted by the filled circle.
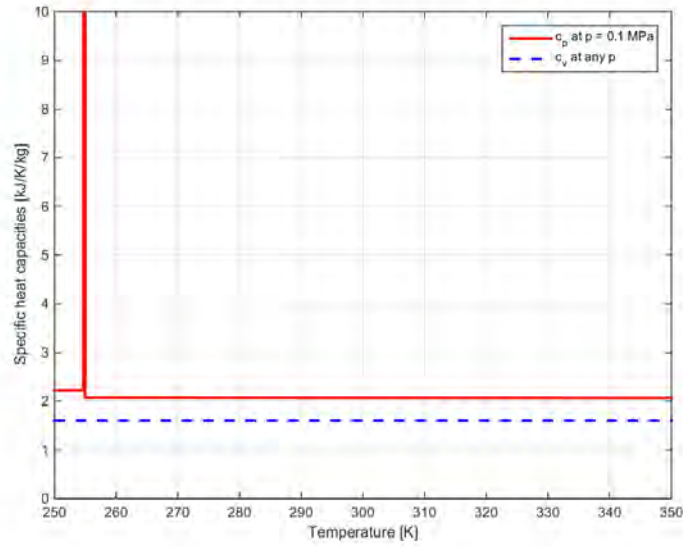
Figure 10:   Specific heat capacities
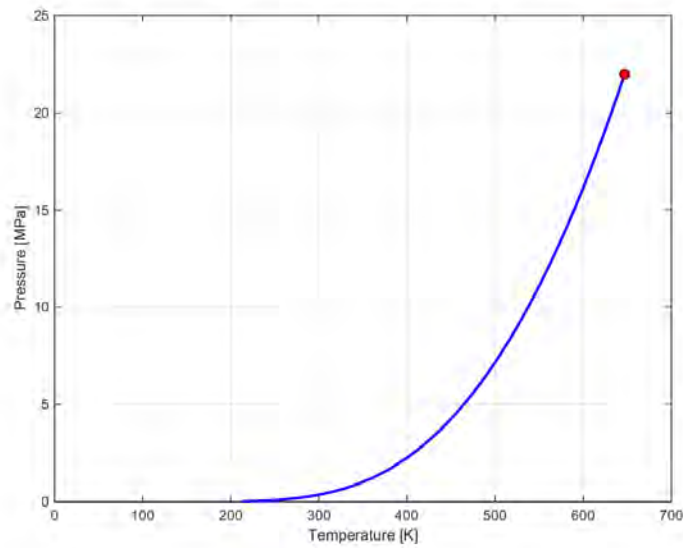
Figure 11:   Vapour pressure curve

The latent heat, energy and work as functions of the absolute temperature are shown in Figure 13. Of course, the sum of the latent energy and work is equal to the latent heat as dictated by (33). All these properties vanish at the critical temperature T_c and beyond.

The van der Waals equation of state does not predict well the phase-transition temperature and pressure of a real fluid from the known specific gas constant R and critical state (T_c, p_c), so its application to the modelling of real-world phenomena is limited. Nevertheless, this

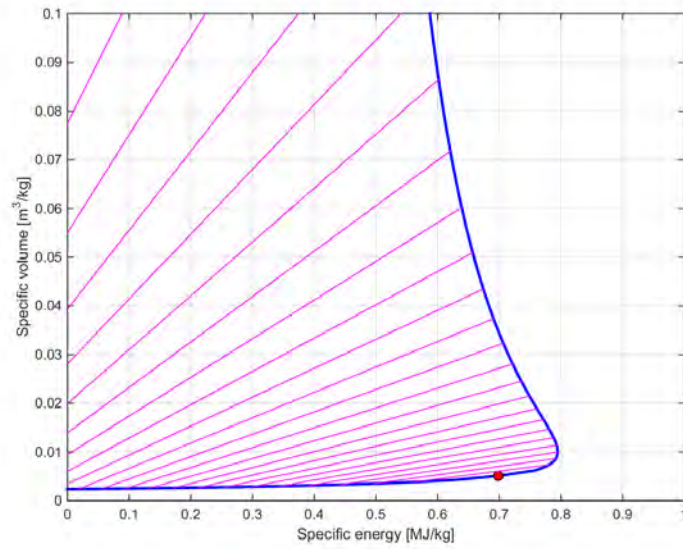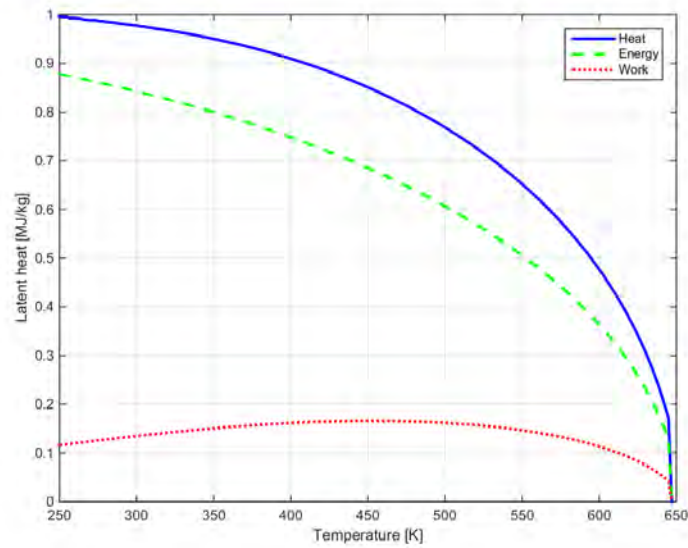*Figure 12: Phase diagram in primary variables*

Figure 13: Latent heat, energy and work

equation of state is an excellent model for theoretical studies, and provides a reasonable model for near critical behaviour of pure liquids and their vapours.

3 Mathematical models

The modelling of phase transitions from the first principles is based on *Thermodynamics* and *Continuum Mechanics*. In this section we formulate the most general model, and discuss several approximations.

3.1 Conservation laws

The conservation laws of continuum mechanics constituting balance of mass, momentum and energy are written in the form [Truesdell 1977]

$$\frac{\partial \rho}{\partial t} + \nabla \cdot (\rho\,\vec{v}) = 0\,, \tag{48}$$

$$\frac{\partial\,(\rho\,\vec{v})}{\partial t} + \nabla \cdot (\rho\,\vec{v} \otimes \vec{v} + P) = \rho\,\vec{f}\,, \tag{49}$$

$$\frac{\partial \varepsilon}{\partial t} + \nabla \cdot (\varepsilon\,\vec{v} + P \cdot \vec{v} + \vec{q}) = \rho\,\vec{f} \cdot \vec{v}\,. \tag{50}$$

Here t is time, $\vec{v}$ velocity, ρ mass density, ε energy density, P momentum flux, $\vec{q}$ heat flux, and $\vec{f}$ external force. The symbol $\otimes$ denotes the tensor product, the centred dot stands for the scalar (inner) product, and ∇ is the gradient operator. The volumetric density of energy is the sum of the internal and kinetic energies, namely

$$\varepsilon = \rho\left(e + \frac{1}{2}\,|\vec{v}|^2\right) \tag{51}$$

where e is the specific internal energy. The balance of angular momentum

$$\frac{\partial\,(\vec{x} \times \rho\,\vec{v})}{\partial t} + \nabla \cdot (\vec{x} \times \rho\,\vec{v} \otimes \vec{v} + \vec{x} \times P) = \vec{x} \times \rho\,\vec{f} \tag{52}$$

requires the momentum flux P to be a symmetric second-rank tensor. Here $\vec{x}$ is the position vector and the symbol $\times$ denotes the vector product. Note that the negative of P is the stress tensor.

In order to complete the governing equations, we need to resort to thermodynamics and rheology. Thermodynamics of compressible fluids unambiguously defines the absolute temperature T and pressure p. For fluids at equilibrium the momentum flux P is expressed in terms of pressure p by the formula

$$P = p\,I \tag{53}$$

where I is the identity tensor. In other words, $P \cdot \vec{n} = p\,\vec{n}$ for any unit vector $\vec{n}$, which is the manifestation of Pascal's law. Of course, at equilibrium the heat flux vanishes: $\vec{q} = \vec{0}$.

Rheological constitutive equations are applicable to irreversible processes due to heat flux and fluid motion. The momentum flux P and heat flux $\vec{q}$ are determined in terms of the

gradients of velocity and temperature. Neglecting reciprocal cross-effects, the momentum flux depends on the deformation-rate tensor $D = (\nabla \vec{v})_{\text{sym}}$ according to Stokes' law

$$P = p\,I - 2\mu\,D \tag{54}$$

where μ is the dynamic coefficient of viscosity (μ is also called the shear coefficient of viscosity to distinguish it from the dilatational coefficient which is usually neglected especially in nearly incompressible flow). The heat flux depends on the temperature gradient according to Fourier's law

$$\vec{q} = -\kappa\,\nabla T \tag{55}$$

where κ is thermal conductivity. The physical properties μ and κ depend on the thermodynamic state of material.

We assume the material is determined by a given dependence of specific entropy s on the specific internal energy e and specific volume $v = 1/\rho$. This assumption is in fact the definition of fluids. A sufficiently small control volume of fluid with nearly uniform distribution of mass and energy is identified with a thermodynamic system attached to the environment, a reservoir of heat and work with the absolute temperature T and pressure p evaluated at the location of the control volume.

We can express the absolute temperature and pressure in terms of the double Legendre transformed entropy

$$T(e,v) = 1 \left/ \frac{\partial \hat{s}(e,v)}{\partial e} \right. , \quad p(e,v) = \frac{\partial \hat{s}(e,v)}{\partial v} \left/ \frac{\partial \hat{s}(e,v)}{\partial e} \right. . \tag{56}$$

It is important to emphasize that the original function $s = s(e,v)$ is not suitable for determining the absolute temperature and pressure, unless it is strictly concave everywhere and hence coincides with $\hat{s}(e,v)$. Alternatively, we can express the primary variables in terms of the Gibbs free energy

$$e(T,p) = g(T,p) - T\frac{\partial g(T,p)}{\partial T} - p\frac{\partial g(T,p)}{\partial p}, \quad \rho(T,p) = 1 \left/ \frac{\partial g(T,p)}{\partial p} \right. . \tag{57}$$

The choice between the representations (56) and (57) for completing the mathematical problem depends on whether one needs to use the primary or potential variables as independent variables.

3.2   Conditions at a strong discontinuity

The conservation laws (48)–(50) are applicable to any flow of a continuum medium, even to flows containing strong discontinuities such as shocks and phase-change fronts. In this case the divergence operator has to be treated in the generalized sense.

The conservation laws of mass, momentum and energy result in the following conditions at the strong discontinuity assumed to be a smooth surface

$$[\rho\,(\vec{v}\cdot\vec{n} - V_n)]_-^+ = 0\,, \tag{58}$$

$$[\rho\,\vec{v}\,(\vec{v}\cdot\vec{n} - V_n) + P\cdot\vec{n}]_-^+ = \vec{0}\,, \tag{59}$$

$$[\varepsilon\,(\vec{v}\cdot\vec{n} - V_n) + \vec{v}\cdot P\cdot\vec{n} + \vec{q}\cdot\vec{n}]_-^+ = 0\,, \tag{60}$$

where $\vec{n}$ is a unit normal vector to the surface, V_n is the speed of propagation of the surface along the normal vector, and the brackets $[\cdot]_-^+$ denote the jump operation

$$[f]_-^+ = f_+ - f_-\,, \qquad f_\pm\,(\vec{x},t) = \lim_{z\to\pm 0} f\,(\vec{x} + z\,\vec{n}(\vec{x},t),t)\,. \tag{61}$$

For example, if the moving strong discontinuity is described implicitly by the equation $F(\vec{x},t) = 0$, then

$$\vec{n} = \frac{\nabla F}{|\nabla F|}\,, \qquad V_n = -\frac{\partial F/\partial t}{|\nabla F|}\,. \tag{62}$$

By the way, the latter formulae provide the continuation of $\vec{n}$ and V_n to the vicinity of the strong discontinuity, so the slightly abused notation for the jump operation in (58)–(60), involving $\vec{n}$ and V_n defined at the surface only, makes sense.

As particular cases the conditions (58)–(60) produce the Rankine–Hugoniot conditions at a shock front [Courant & Friedrichs 1948] and the Stefan condition at a phase-change front [Meirmanov 1992]. The Stefan condition is derived by assuming zero velocity. This immediately demands that density is continuous across the phase-change front: $[\rho]_-^+ = 0$. Therefore, since $\rho = \rho_+ = \rho_-$, the energy balance condition (60) reduces to the Stefan condition

$$[\varepsilon]_-^+\,V_n \equiv \rho\,[e]_-^+\,V_n = [\vec{q}\cdot\vec{n}]_-^+\,. \tag{63}$$

In the classical formulation of the Stefan problem that involves tracking the phase-change front, the absolute value of the jump of the specific internal energy e across the phase-change front is equal to δe, the specific latent heat of phase transition.

3.3 The Stefan problem

The general governing equations reduce to the Stefan problem by assuming zero velocity and constant density. Such a situation arises when the solid phase is at rest and an incompressible liquid phase is of the same density as the solid phase and does not move during the process of solidification or fusion.

The mass and momentum conservation laws are automatically satisfied, so the only non-trivial equation is the balance of energy which reduces to

$$\frac{\partial\varepsilon}{\partial t} = \nabla\cdot(\kappa\,\nabla T) \tag{64}$$

where $\varepsilon = \rho\, e$ with constant density ρ. The Stefan condition (63) along with the condition for fusion temperature is specialized to the equations at the phase-change front

$$[\varepsilon]_-^+ \, V_n + \left[\kappa\, \frac{\partial T}{\partial n}\right]_-^+ = 0\,, \quad T_+ = T_- = T_*\,. \tag{65}$$

Assuming given dependences $\varepsilon = \varepsilon(T)$ and $\kappa = \kappa(T)$, we end up with the classical formulation of the Stefan problem in which the location of the phase-change front is part of solution.

There are many numerical schemes aimed at an accurate solution to the classical Stefan problem, however their application to real-world problems is limited. This is because the tracking of the phase-change front is tedious as the front can change topology with evolving time. Indeed, the fronts can grow from nothing (new phase nucleation), merge, break and disappear altogether. So, it is desirable to provide a uniform formulation of the Stefan problem which does not involve tracking the phase-change fronts explicitly, and can be employed in Computational Fluid Dynamics (CFD) simulation of real-world problems in a straightforward manner.

3.3.1   Fictitious capacity method

Let us introduce the volumetric heat capacity $\eta = \rho\, c_p$ which is equal to the derivative of the volumetric internal energy

$$\eta(T) = \frac{\mathrm{d}\varepsilon(T)}{\mathrm{d}T}\,. \tag{66}$$

The energy-balance equation is specialized to the classical heat conduction equation with variable coefficients

$$\eta(T)\, \frac{\partial T}{\partial t} = \nabla \cdot [\kappa(T)\, \nabla T]\,. \tag{67}$$

When phase transitions take place the volumetric heat capacity exhibits a delta-function singularity at $T = T_*$.

In order to avoid this problem, we approximate the coefficient $\eta(T)$ in (67) by the centred finite difference

$$\eta(T) = \frac{\varepsilon\,(T + \delta T/2) - \varepsilon\,(T - \delta T/2)}{\delta T} \tag{68}$$

where δT is some regularization parameter. It is natural to call this regularization the fictitious-capacity approximation. The advantage of this formulation is in the fact that there is no need to track the phase-transition front. It is conceivable that the regularization parameter δT could be neither very small nor very large, so there arises the problem of an optimal choice of δT.

Many efficient numerical algorithms are designed for solution of the problem (67), however, all of them are not conservative in nature because the balance of energy is not approximated exactly. Due to the fictitious-capacity regularization, implicit numerical schemes can be applied to this class of problems. Finite Element Method (FEM) is a good choice for numerical solution of the Stefan problem in temperature formulation.

3.3.2 Enthalpy formulation

The alternative 'enthalpy' formulation is in terms of energy

$$\frac{\partial \varepsilon}{\partial t} = \nabla \cdot [\kappa(\varepsilon)\, \nabla T(\varepsilon)] \tag{69}$$

where the thermal conductivity $\kappa(\varepsilon)$ is now a given function of energy. Note that this formulation requires a suitable interpolation of the thermal conductivity κ over the range of energies corresponding to the thermodynamic states of phase coexistence, namely, where $T(\varepsilon) = T_*$. Of course, the previous temperature dependence $\kappa(T)$ can be superposed with $T(\varepsilon)$ to obtain the desired dependence but this boils down to determining κ at the fusion temperature T_*.

The enthalpy formulation allows one to design conservative numerical schemes. Usually, such schemes are explicit as the problem degenerates at $T(\varepsilon) = T_*$. Finite Volume Method (FVM) is well suited to this formulation.

3.3.3 Exact similarity solution

The exact solution to the Stefan problem we are going to describe has the following physical interpretation. At time $t = 0$ two phases of a substance occupy two half-planes, $\{x > 0\}$ and $\{x < 0\}$, are kept at constant temperatures $T_\pm^\infty$, and have temperature-independent thermal conductivities $\kappa_\pm$ and volumetric heat capacities $\eta_\pm$. Here the 'plus' and 'minus' subscripts correspond to the positive and negative values of x, respectively. The phase-transition temperature T_* is implied to be between T_-^∞ and T_+^∞. The latent heat of fusion per unit volume is $\delta\varepsilon = \rho\, \delta e$.

The front position is defined by the law $x = 2\lambda\sqrt{t}$ with some λ to be determined. The following similarity solution satisfies the heat conductivity equation [Hill 1987]

$$T(x, t) = T_\pm^\infty + \left(T_* - T_\pm^\infty\right) \frac{\operatorname{erfc}\left(\pm\sqrt{\eta_\pm/\kappa_\pm}\,\xi\right)}{\operatorname{erfc}\left(\pm\sqrt{\eta_\pm/\kappa_\pm}\,\lambda\right)}, \quad \xi = \frac{x}{2\sqrt{t}}, \tag{70}$$

where the 'plus' and 'minus' subscripts are now taken for $x > 2\lambda\sqrt{t}$ and $x < 2\lambda\sqrt{t}$, respectively, and

$$\operatorname{erfc}(x) = \frac{2}{\sqrt{\pi}} \int_x^\infty \exp\left(-x^2\right)\, \mathrm{d}x \tag{71}$$

is the complementary error function. For $t > 0$, the temperature $T(x, t)$ is continuous everywhere, tends to $T_\pm^\infty$ as $x \to \pm\infty$, and approaches T_* at the phase-change front. It is straightforward to check that the Stefan condition at the phase-change front $x = 2\lambda\sqrt{t}$ results in the transcendent equation

$$\operatorname{sgn}\left(T_+^\infty - T_-^\infty\right)\delta\varepsilon\,\lambda + \frac{\left(T_+^\infty - T_*\right)\sqrt{\eta_+\,\kappa_+}}{\Phi\left(+\sqrt{\eta_+/\kappa_+}\,\lambda\right)} + \frac{\left(T_-^\infty - T_*\right)\sqrt{\eta_-\,\kappa_-}}{\Phi\left(-\sqrt{\eta_-/\kappa_-}\,\lambda\right)} = 0 \tag{72}$$

where $\Phi(x) = \sqrt{\pi}\,\exp\left(x^2\right)\,\mathrm{erfc}(x)$, the scaled complementary error function with asymptotic behaviour $\Phi(x) \approx 1/x$ as $x \to +\infty$.

The transcendent equation (72) has a unique solution λ which can be obtained numerically in an efficient way. This exact solution is used as a benchmark to test numerical schemes.

3.3.4   Verification of uniform numerical schemes

Verification is the process of evaluating a numerical scheme against a benchmark solution. This process should not be confused with validation which is the process of testing a model against real-world experiments. A particular model can pass verification but fail validation, for example, because the underlying mathematical model may not include all the essential physical effects.
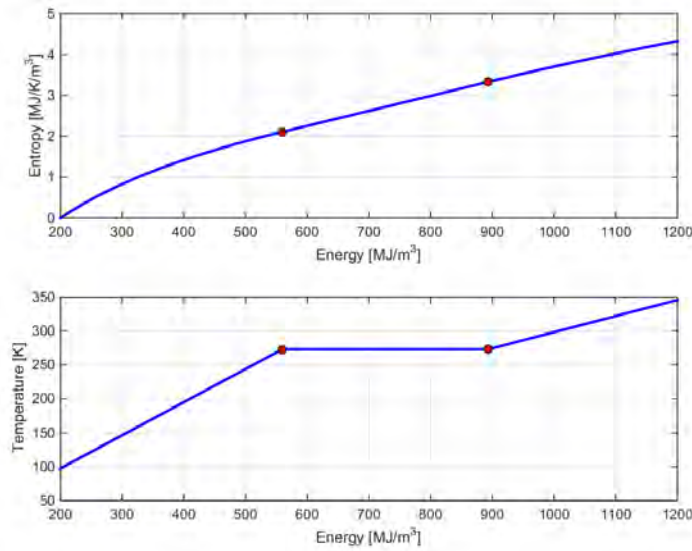

Figure 14:   Entropy and temperature of the ice-water system versus volumetric energy

The exact similarity solution is used to verify the explicit conservative scheme and the implicit fictitious-capacity scheme. The material is the ice-water system at standard pressure with the following physical properties [Lide 1999]:

- fusion (melting) temperature $T_* = 273\,\mathrm{K}$,

- volumetric latent heat $\delta\varepsilon = 334\,\mathrm{MJ/m^3}$,

- volumetric heat capacity of ice $\eta_s = 2.05\,\mathrm{MJ/m^3/K}$,

- volumetric heat capacity of water $\eta_l = 4.22\,\mathrm{MJ/m^3/K}$,

- thermal conductivity of ice $\kappa_s = 2.18\,\mathrm{W/m/K}$,

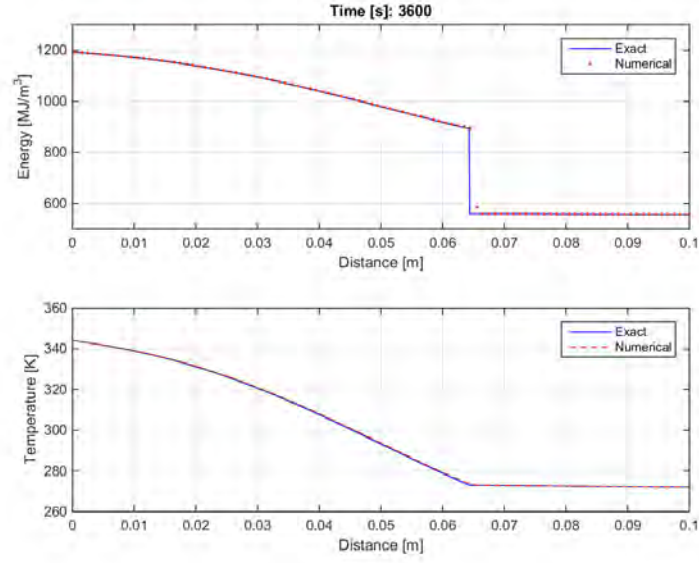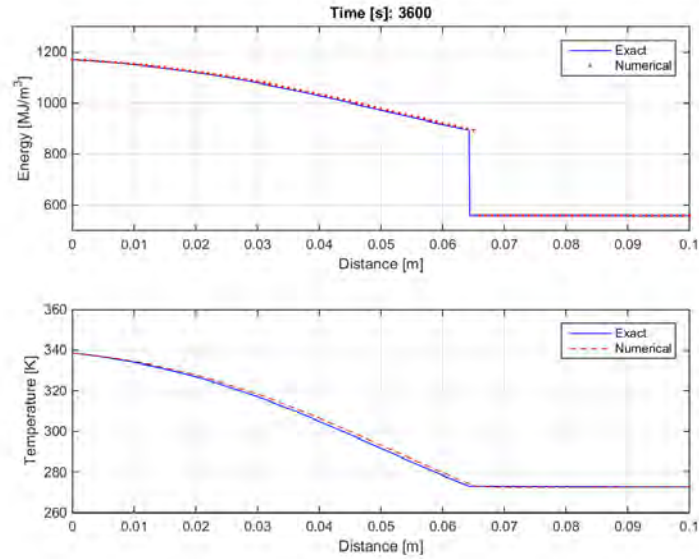- thermal conductivity of water $\kappa_l = 0.56\,\mathrm{W/m/K}$.

Figure 15: Conservative scheme

Figure 16: Fictitious-capacity scheme: $\delta T = 1\,\mathrm{K}$

The dependences $s = \hat{s}(\varepsilon)$ and $T = T(\varepsilon)$ are shown in Figure 14.

In numerical simulations the following values for the parameters defining the benchmark solution are taken: $\kappa_- = \kappa_l$, $\kappa_+ = \kappa_s$, $\eta_- = \eta_l$, $\eta_+ = \eta_s$, $T_-^\infty = 350\,\mathrm{K}$ and $T_+^\infty = 270\,\mathrm{K}$. The spatial interval is $\{0\,\mathrm{m} \le x \le 0.1\,\mathrm{m}\}$, the phase-transition front is located at the middle $x = 0.05\,\mathrm{m}$, and the initial temperature is piecewise constant (this corresponds to $t = 0$ of the similarity solution). The Dirichlet boundary conditions at both ends of the
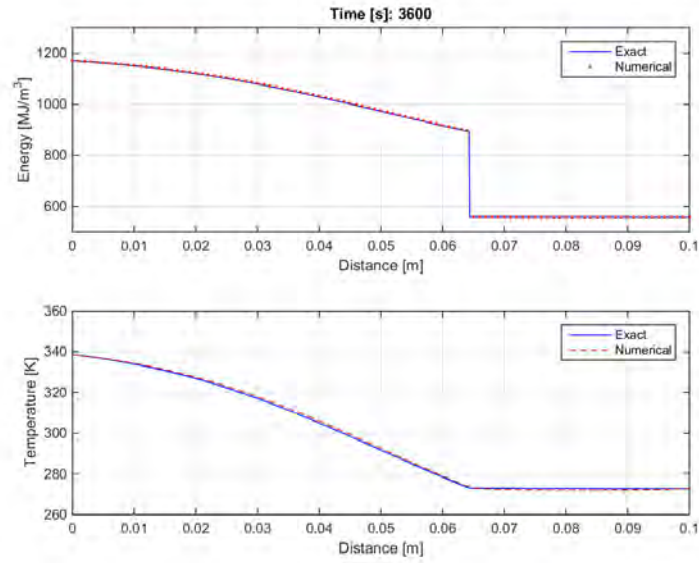
Figure 17: Fictitious-capacity scheme: $\delta T = 2\,\mathrm{K}$
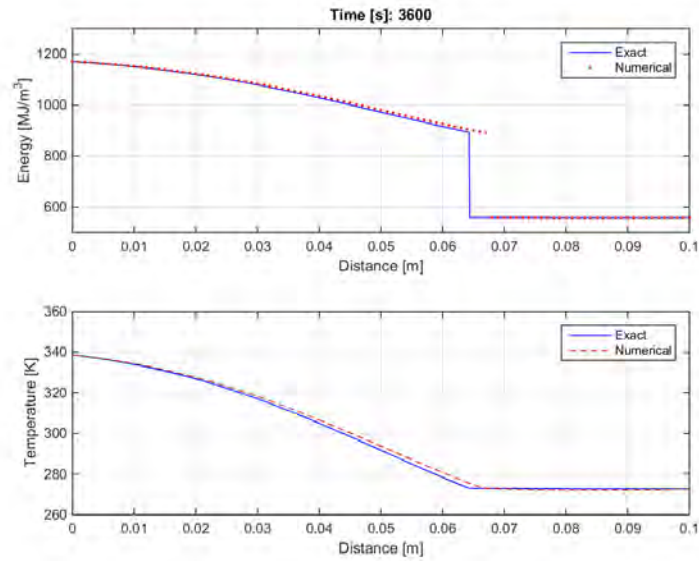
Figure 18: Fictitious-capacity scheme: $\delta T = 4\,\mathrm{K}$

spatial interval are maintained according to the values given by the exact solution. The spatial interval is discretized by 100 evenly spaced points for both explicit conservative and implicit fictitious-capacity schemes.

Figure 15 shows the numerical solution obtained with the conservative scheme. It is seen a good approximation of the temperature field and satisfactory resolution of the position of the phase-change front at the final time.

Figures 16–18 show the numerical solution obtained with the implicit fictitious-capacity scheme (with timestep $\tau = 1\,\mathrm{s}$) for $\delta T = 1\,\mathrm{K}$, $\delta T = 2\,\mathrm{K}$ and $\delta T = 4\,\mathrm{K}$, respectively. As a general fact, non-conservative schemes do not predict the position of a strong discontinuity well, and this is evident for $\delta T = 1\,\mathrm{K}$ and particularly for $\delta T = 4\,\mathrm{K}$. The optimal choice of the regularization parameter is $\delta T = 2\,\mathrm{K}$ but this choice is not universal as it may change in other configurations.

3.4 Models for two-parametric phase transitions

The most general model of phase transitions in fluids written in the primary (conservative) variables directly utilizes the conservation laws (48)–(50) where the potential variables given by (56) appear in the constitutive equations (54) and (55). The main difficulty is associated with the fact that the mapping (56) degenerates at the phase-coexistence states, and therefore only explicit algorithms can be effectively applied. There is also a challenge to implement the double Legendre transform of entropy, and eventually produce (56), which has to be correlated with the experimentally obtained vapour pressure curve and latent heat of the material in question.

Finite Volume Method (FVM) is well suited to tackle this type of problem. The implementation of an explicit conservative scheme is straightforward. Discretize the computational domain into a collection of control volumes (cells) separated by facets oriented by normal vectors, assign primary variables to each cell and calculate normal fluxes between neighbouring cells. Choose a timestep small enough to preserve numerical stability and update the solution at the next time level. The main problem is associated with an accurate evaluation of fluxes between two cells in contact without introducing numerical instability. Such conservative schemes are uniform as there is no need to track the phase-change fronts.

A uniform scheme can be designed in potential variables as well. However, such schemes are not conservative in nature. Using (57) and the definitions of heat capacity, compressibility and expansivity, the governing equations take the form

$$a_T \left(\frac{\partial p}{\partial t} + \vec{v} \cdot \nabla p \right) - b_p \left(\frac{\partial T}{\partial t} + \vec{v} \cdot \nabla T \right) + \nabla \cdot \vec{v} = 0 \,, \tag{73}$$

$$\rho \left(\frac{\partial \vec{v}}{\partial t} + \vec{v} \cdot \nabla \vec{v} \right) + \nabla p - \nabla \cdot (2\mu\, D) = \rho\, \vec{f}, \tag{74}$$

$$\rho\, c_p \left(\frac{\partial T}{\partial t} + \vec{v} \cdot \nabla T \right) - T\, b_p \left(\frac{\partial p}{\partial t} + \vec{v} \cdot \nabla p \right) = \nabla \cdot (\kappa\, \nabla T) + 2\mu\, D : D \,. \tag{75}$$

As in the Stefan problem, the main difficulty is caused by the discontinuous dependences (57) which results in delta-function singularities of the heat capacity c_p, compressibility a_T and expansivity b_p.

Following the spirit of the fictitious-capacity method, we approximate these coefficients by the finite differences

$$c_p = T\, \frac{s\,(T + \delta T/2, p) - s\,(T - \delta T/2, p)}{\delta T} \,, \tag{76}$$

$$a_T = \frac{\log\left[\, v\left(T, p - \delta p/2\right)/\, v\left(T, p + \delta p/2\right)\right]}{\delta p}\,, \tag{77}$$

$$b_p = \frac{\log\left[\, v\left(T + \delta T/2, p\right)/\, v\left(T - \delta T/2, p\right)\right]}{\delta T}\,, \tag{78}$$

where δT and δp are some regularization parameters of dimension of temperature and pressure, respectively, and $s(T, p)$ and $v(T, p)$ are expressed in terms of $g(T, p)$. The problem of an optimal choice for the regularization parameters arises.

3.4.1 Lubrication theory approximation

The system of equations (73)–(75) for the potential variables (T, p) and velocity $\vec{v}$ is of a mixed type. In the lubrication theory approximation this system of equations can be reduced to a parabolic system of equations. This approximation is valid for fluid flow in thin gaps and tubes as well as in a porous medium.

For the sake of simplicity, let us neglect the external force $\vec{f}$. For a slow viscous flow, the solution to the momentum balance equation can be approximated by Darcy's law

$$\vec{v} = -\phi\,\nabla p \tag{79}$$

where fluidity ϕ satisfies the Poisson equation

$$\nabla \cdot (\mu\,\nabla\phi) + 1 = 0\,. \tag{80}$$

Equation (80) generalizes the Hele–Shaw flow. Due to adherence condition for velocity, the fluidity ϕ must vanish at contact with a rigid body, such as a container wall. In porous media, the fluidity ϕ becomes a given coefficient of filtration after the procedure of homogenization. In this case the conservation laws must be modified to include porosity.

With this simplification the conservation laws of energy and mass reduce to the system of convection-diffusion equations

$$C_{ij}\left(\frac{\partial u_j}{\partial t} + \vec{v}\cdot\nabla u_j\right) = \nabla \cdot (K_{ij}\,\nabla u_j) + F_i \tag{81}$$

where

$$C = -\begin{bmatrix} \dfrac{\partial^2 g}{\partial T^2} & \dfrac{\partial^2 g}{\partial T\,\partial p} \\[4mm] \dfrac{\partial^2 g}{\partial T\,\partial p} & \dfrac{\partial^2 g}{\partial p^2} \end{bmatrix}, \quad K = \begin{bmatrix} \dfrac{\kappa}{T} & 0 \\[4mm] 0 & \phi \end{bmatrix}, \tag{82}$$

$$u = \begin{bmatrix} T \\[2mm] p \end{bmatrix}, \quad F = \begin{bmatrix} \dfrac{2\mu\,D:D}{T} + \dfrac{\kappa\,|\nabla T|^2}{T^2} \\[4mm] 0 \end{bmatrix}, \tag{83}$$

and the velocity $\vec{v}$ is expressed by Darcy's law (79). The 'capacity' matrix C and 'conductivity' matrix K are symmetric and positive definite, and hence the governing equations form a parabolic system of equations.

This system of equations is not standard. Indeed, the fluidity ϕ is part of the solution and must satisfy (80) with a zero boundary condition at the solid-fluid interface. In particular, the matrix K degenerates near this boundary, causing problems in numerical simulation. Also, the matrix C has delta-function singularities at the phase-transition curve and has to be regularized, for example, by centred differences. This procedure results in large variation of the capacity coefficients that may cause problems as well. Finally, the velocity field is not given but depends on the solution.

The advantage of this symmetric form of the parabolic system of equations is in the fact that C and K can be diagonalized simultaneously. This fact is important for designing a stable numerical scheme for diffusion-convection flow using artificial balancing diffusion. The algorithm is based on the solution of the characteristic equation

$$|C - \lambda\,K| = 0 \tag{84}$$

for generalized eigenvalues λ, and then finding the matrix of generalized eigenvectors E. It is guaranteed that we get two positive generalized eigenvalues from which we form the diagonal matrix

$$\Lambda = \left[\begin{array}{cc} \lambda_+ & 0 \\ 0 & \lambda_- \end{array} \right] \tag{85}$$

and represent

$$C = K\,E\,\Lambda\,E^{-1}\,. \tag{86}$$

The artificial balancing diffusion matrix is given by the formula

$$A = K\,E\,\delta\,(\Lambda)\ E^{-1} \tag{87}$$

where

$$\delta\,(\Lambda) = \left[\begin{array}{cc} \delta\,(\mathrm{Pe}_+) & 0 \\ 0 & \delta\,(\mathrm{Pe}_-) \end{array} \right]\,. \tag{88}$$

Here $\delta(x) = x\,\coth(x) - 1$ is the transcendent function appearing in scalar convection-diffusion equation, $\mathrm{Pe}_\pm = h\,\lambda_\pm\,|\vec{v}|$ are the local Péclet numbers, and h is the finite element size in the direction of velocity. Anisotropic diffusion is controlled by the dyad $\vec{v} \otimes \vec{v}$ to reduce excessive cross-wind numerical diffusion. This procedure generalizes the Streamline Upwind Petrov–Galerkin (SUPG) method [Donea & Huerta 2003] to convection-diffusion systems of equations.

3.4.2 Simulation results

Consider a one-dimensional viscous flow of fluid modelled by the van der Waals equation of state, in the lubrication theory approximation. The initial state of the fluid in the liquid

phase is uniform (constant temperature and pressure), and the flow is caused by a gradual increase of temperature at the left solid wall. The right wall is permeable and insulated, where pressure is kept at the initial reference pressure, so the fluid will start moving in the right direction due to a pressure gradient.
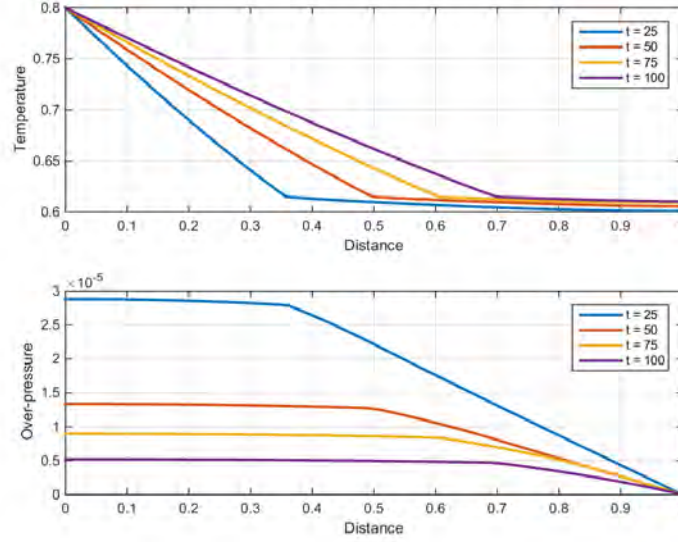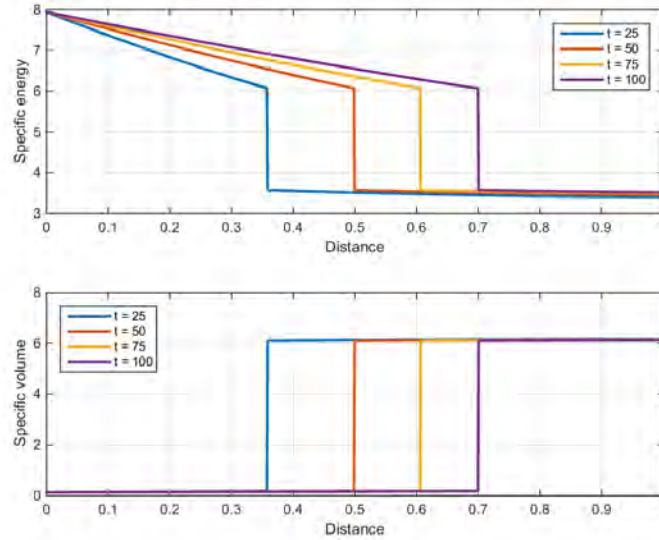

Figure 19:   Temperature and over-pressure.

Figure 20:   Specific energy and volume.

We employ dimensionless variables in the van der Waals equation of state which correspond to $R = 1$, $c_v = 10$, $T_c = 1$ and $p_c = 1$. The initial reference temperature and pressure
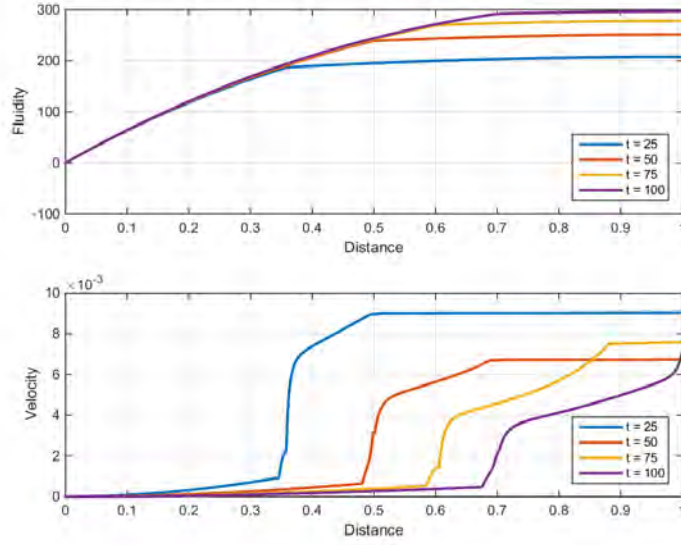
Figure 21: Fluidity and velocity.

are equal to $T_0 = 0.6$ and $p_0 = 0.1$, respectively. The viscosity and thermal conductivity depend on the specific volume according to the formulae $\mu(v) = 0.01\sqrt{v_0/v}$ and $\kappa(v) = 0.1\sqrt{v_0/v}$ where v_0 is the specific volume at this reference state. At the left boundary $x = 0$ of the spatial interval $\{0 < x < 1\}$ the onset temperature is imposed which linearly increases from the initial value T_0 to $T_1 = 0.8$ within the time interval $0 \le t \le 1$ and then kept constant up to the final time $t = 100$. At the right boundary $x = 1$, pressure is equal to p_0 and the Neumann condition (zero heat flux) is imposed for temperature. For fluidity, the Dirichlet condition $\phi = 0$ is imposed at $x = 0$ and the Neumann condition at $x = 1$. Note that the Neumann condition is natural in FEM. The spatial interval is discretized by 1000 points, and the regularization parameters are equal to $\delta T = 0.01$ and $\delta p = 0.01$.

A fully vectorized FEM code is developed in MATLAB®. In order to achieve numerical stability, second-order integration in time is implemented with iterations to update the wildly varying nonlinear coefficients of the governing equations. The briefly described SUPG method is used to add artificial balancing diffusion to the discretized transport terms in the parabolic system of equations (81).

The distribution of temperature and over-pressure $(p - p_0)$ are shown in Figure 19, and the specific energy and volume are depicted in Figure 20. As is expected, the potential variables are continuous whereas the primary variables exhibit a discontinuous behaviour. The fluidity and velocity shown in Figure 21 are also continuous, though velocity exhibits quite a steep slope near the phase-transition front.

4   Discussion

In *Continuum Mechanics* the primary variables appear in the conservation laws of mass and energy, whereas entropy is a new concept that leads to the definition of the absolute temperature and pressure. In this paper we apply a consistent methodology for modelling phase transitions using the Gibbs free energy defined by the Legendre transform of entropy (18) as opposed to the traditional definition (17). This approach immediately provides us with a bunch of important consequences, such as the global continuity and concavity of the Gibbs free energy that resulted in the positivity of specific heat capacities and compressibility, and the relations (35) for the latent energy and volume in terms of the latent entropy and vapour pressure curve.

In many textbooks, fluids are defined as substances whose stress tensor at equilibrium is spherical [Batchelor 1967, Prandtl 1967], or, equivalently, for which Pascal's law (53) widely used in hydraulics is valid.[4] Methodologically, it is more natural to define fluids as substances described by a two-parametric thermodynamic system taking the specific internal energy and volume as primary variables. All the distinguishing properties of fluids can be deduced from the known dependence $s = s(e, v)$ using the *Maximum Entropy Principle*. It is worthwhile noting that capillary fluids can be modelled by assuming that entropy additionally depends on the gradient of density [de Sobrino 1976, Antanovskii 1996] or some other order parameter.

A priori the entropy dependence on the primary variables, $s = s(e, v)$, can be quite arbitrary. This is the fundamental equation of state defining a particular substance. However, the dependence $g = g(T, p)$ must always be a continuous concave function as the manifestation of the *Maximum Entropy Principle*, and it will be a serious mistake to model a particular phenomenon assuming this function to be given in an arbitrary fashion.

It is emphasized that, when modelling fluid flows with phase transitions, it is more consistent to use the double Legendre transform (24) beforehand as the fundamental equation of state. This is particularly useful when modelling phase transitions numerically using an explicit conservative scheme.

The final remark is related to the fact that the 'capacity' and 'conductivity' matrices are symmetric and positive definite. This important observation allows us to symmetrize the governing equations in the lubrication theory approximation similarly to the symmetrization procedure applied to the thermo-diffusive Stefan problem which models phase transitions in materials with a small concentration of impurity [Antanovskii 1992]. In this case the absolute temperature and chemical potential are the potential thermodynamic variables. Symmetrization of the governing equations of heat transfer relies on a symmetric form of the 'conductivity' matrix which is guaranteed by the *Minimum Entropy Production Principle*. Since two symmetric positive definite matrices can be simultaneously diagonalized, many results obtained for a scalar convection-diffusion equation are extended to matrix convection-diffusion equations.

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[4]This is true when the effects of capillarity are neglected.

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19. ABSTRACT

Phase transitions occur in a variety of physical phenomena ranging from condensation of gases to solidification of liquids. It is of paramount importance to provide an adequate modelling of these phenomena in a thermodynamically consistent way. This paper addresses an introduction into the mathematical modelling of phase transitions in fluids from the perspective of consistently employing a modified Legendre transform of entropy considered as a given function of internal energy and volume. An explicit conservative scheme for incompressible phase transition and an implicit non-conservative scheme based on the fictitious-capacity and lubrication-theory approximations are implemented in MATLAB$^{\circledR}$. Illustrative numerical simulations are conducted, and some results are verified against an exact benchmark solution.